

AD-A050 638

NAVAL SURFACE WEAPONS CENTER WHITE OAK LAB SILVER SP--ETC F/G 7/3
COMPATIBILIZATION OF POLYPHENYLQUINOXALINE WITH OTHER POLYMERS --ETC(U)
NOV 77 I ANGRES
NSWC/WOL/TR-77-118

UNCLASSIFIED

1 OF 1
ADA
050838



END
DATE
FILMED
4 -78
DDC

NL



AD No. **DDC FILE COPY, AD A 050638**

NSWC/WOL TR 77-118

2

12

COMPATIBILIZATION OF POLYPHENYLQUIN- OXALINE WITH OTHER POLYMERS USING CHLOROFORM AS THE SOLVENT IN THE PREPARATION OF POLYMERIC MEMBRANES

BY ISAAC ANGRES

RESEARCH AND TECHNOLOGY DEPARTMENT

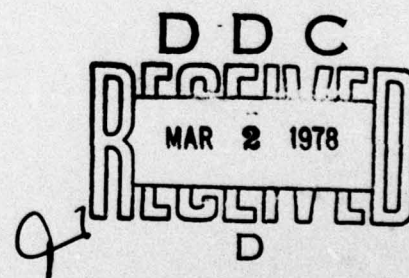
16 NOVEMBER 1977

Approved for public release, distribution unlimited



NAVAL SURFACE WEAPONS CENTER

Dahlgren, Virginia 22448 • Silver Spring, Maryland 20910



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC/WOL/TR-77-118	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) COMPATIBILIZATION OF POLYPHENYLQUINOXALINE WITH OTHER POLYMERS USING CHLOROFORM AS THE SOLVENT IN THE PREPARATION OF POLYMERIC MEMBRANES.		5. TYPE OF REPORT & PERIOD COVERED Compatibility Study rept. Dec 1976 - Jun 1977
6. AUTHOR Isaac/Angres		7. PERFORMING ORG. REPORT NUMBER
8. CONTRACT OR GRANT NUMBER(s)		9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62543N: F43431 SF 43431302 CR33 BB501
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center White Oak Laboratory White Oak, Silver Spring, Maryland 20910		10. REPORT DATE 16 Nov 77
11. CONTROLLING OFFICE NAME AND ADDRESS		11. NUMBER OF PAGES 80
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. SECURITY CLASS. (of this report) Unclassified
		13a. DECLASSIFICATION/DOWNGRADING SCHEDULE
14. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
15. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
16. SUPPLEMENTARY NOTES		
17. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polymer membranes, Compatibilization Polyphenylquinoxaline, Chloroform		
18. ABSTRACT (Continue on reverse side if necessary and identify by block number) This work was performed to determine if polyphenylquinoxaline (PPQ) can be made compatible with other polymers such as polyvinylacetate, polyvinylpyrrolidone, vinylpyrrolidone/vinylacetate copolymer, cellulose acetate, cellulose triacetate, and polybrene. The primary purpose was to prepare homogeneous solution blends containing PPQ combined with one, two or three of the above polymers. Such solution blends were used to prepare polymeric membranes to be used as battery separators.		

DD FORM 1473

1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

391 596

Hm

SUMMARY

This investigation was undertaken to develop a method of compatibilizing polyphenylquinoxaline (PPQ) with polymers such as polyvinylpyrrolidone (PVP), cellulose acetate, cellulose triacetate, polyvinyl acetate and polybrene. Such compatibilization is achieved by using chloroform as the solvent and the resulting blends are used for preparing membranes useful as battery separators. This work is being performed under NAVSEA Task Number SF43431302.

J. R. DIXON
By direction

ADDITION for	
DTIC	White Section <input checked="" type="checkbox"/>
DDC	Soft Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	AVAIL. and/or SPECIAL
A	

DDC
RECEIVED
MAR 2 1978
D

CONTENTS

	Page
INTRODUCTION	3
EXPERIMENTAL	3
Polymer Preparation	3
Membrane Preparation	4
DISCUSSION	5
SUMMARY	6

ILLUSTRATIONS

Figure		Page
1	Hydrogen Bonded Interaction of PPQ with Chloroform	5

INTRODUCTION

Earlier investigations¹ on the development of polymeric membranes based on polyphenylquinoxalines (PPQ), had as the leachable additive polyvinylpyrrolidone and m-cresol as the solvent. However, the use of m-cresol as the solvent is somewhat cumbersome because of its high boiling point. In addition, when the need to use other leachable additives arose, we encountered a problem of polymer-polymer compatibilization when m-cresol was used as the solvent.

It is known that the unique characteristics of homopolymers and copolymers are conferred by their specific chemical and stereo-structures, by their molecular weight distribution, and by their intra- and inter-chain interactions. Although such homogeneous materials have numerous useful chemical and physical properties, it is often desirable to seek improvements (i.e., lower their inherent electrical resistance) in their characteristics or processing requirements. In order to accomplish the above improvements one finds that it is necessary to prepare multicomponent polymer systems. Thus, homogeneous blends (in solution) comprising mixtures of polymers, provide a route to combinations of properties not otherwise available.

In this study our efforts focused on the preparation of homogeneous solution blends in chloroform. The above blends contain PPQ as the main polymer and other resins such as polyvinylacetate, polyvinylpyrrolidone, vinylacetate/vinylpyrrolidone copolymer, cellulose acetate, cellulose triacetate, and polybrene (a diquatamary ammonium bromide polymer). The use of chloroform as the solvent solves the problem of PPQ compatibilization with other polymers in m-cresol. Similarly, it will be noted that preparation of the membranes is faster because of the ease of evaporation of the solvent.

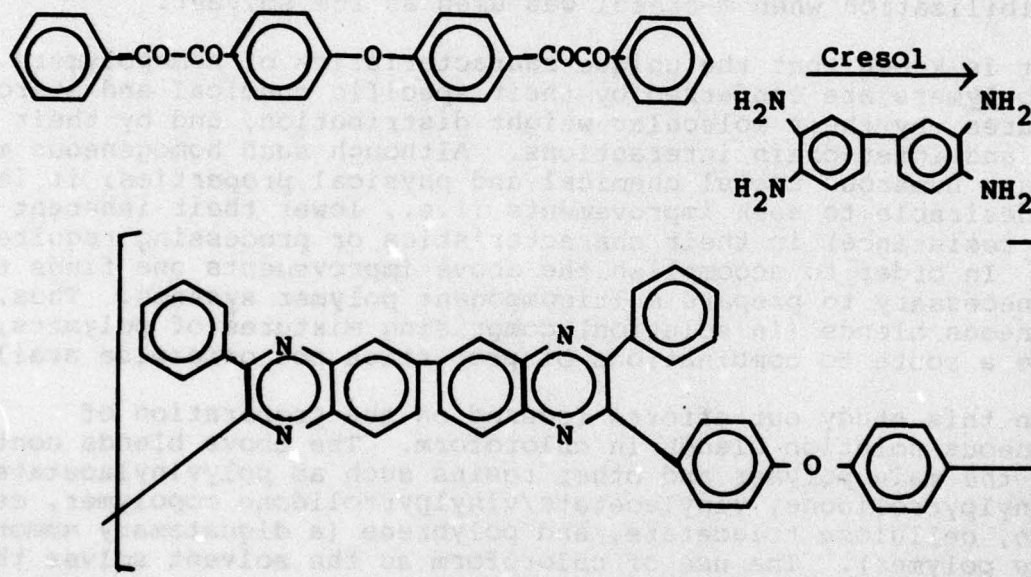
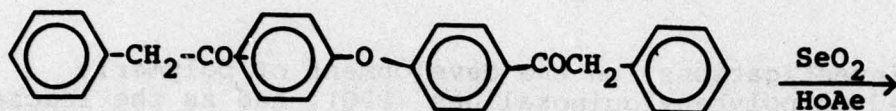
EXPERIMENTAL

POLYMER PREPARATION

Poly-2,2'-(p,p'-oxydiphenylene)-6,6'-Di(3-phenylquinoxaline)

The PPQ based polymer used in the preparation of the membranes for this study was purchased as a 10% solution in m-cresol from the Narmco Division of the Whittaker Corporation. The synthetic route to prepare this polymer is as follows:

1. W. P. Kilroy and J. V. Duffy, "Development of an improved separator Material for Alkaline-Silver-Zinc batteries", NSWC/TR-76-135 White Oak, Maryland, February 1977.



The reported inherent viscosity for this polymer is 2.05 $\frac{\text{dl}}{\text{g}}$ and the glass transition temperature is 693°K (420°C)². Polyvinylacetate (low, medium, and high molecular weight), polyvinylacetate/vinyl pyrrolidone copolymer, polybrene, polyvinylpyrrolidone, cellulose acetate, and cellulose triacetate were all obtained from Aldrich Chemical Company.

MEMBRANE PREPARATION

The following procedure applies to all of the above polymers, when blended with the PPQ and using chloroform as the solvent:

2. P. Hergenrothen and H. Levine, J. Polymer Science A-1 5 1453(1976)

30 g of the 10% PPQ solution is added to a suitable container followed by 2 g of any of the above polymers or 2 g of a mixture of the above polymers. To the above mixture there is added 100 ml of chloroform and the resulting composition is stirred thoroughly until a homogeneous solution is obtained. The homogeneous solution is used for casting purposes.

The membranes are prepared by spreading the homogeneous solution onto a glass plate (16 cm X 28 cm X 0.9 cm) with a metal bar. The thickness of the final film was controlled by means of masking tape which was placed along the edges of the glass plate (3 layers of tape \approx 1 mil thickness). It was found necessary to thoroughly wash the glass plate with water and detergent and then to rinse with isopropyl alcohol to insure good wetting by the polymer solutions.

Following the casting of the film, the solvent (chloroform) is allowed to evaporate slowly for about 2-3 minutes by partially enclosing the plate with a plastic container, and then immersing the plate in a 50:50 methanol-water bath, and allowing to stand for 10 minutes. The film is washed with water and dried in air. Films obtained by this method have good handleability and do not shrink on drying.

The leachable additives are either extracted with water or hydrolyzed in KOH (45%) at 80°C to create porosity. (The full characterization and the effect of hydrolysis on resistance will be the subject of another report to be published at a later date).

DISCUSSION

Incompatibility (insolubility) is an often encountered problem that prevents the preparation of useful blends. The use of chloroform as the solvent allows for the preparation of many and useful PPQ polyblends in solution. A plausible explanation as to why chloroform acts as a good compatibilizing agent is accounted by weak hydrogen bonding with the PPQ, as shown in Figure 1.

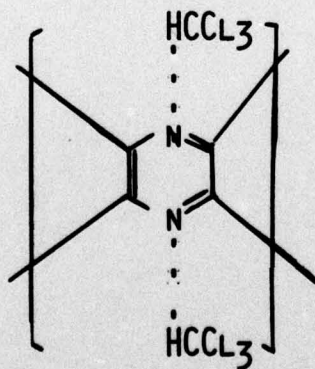


Figure 1. Hydrogen-bonded Interaction of PPQ with Chloroform.

By tying up all the PPQ by means of this hydrogen bonding interaction one can then dissolve other polymers in the same system without encountering the problem of precipitation when mixing two or more polymers.

The use of chloroform also allows one to make all the possible mathematical combinations by mixing all of the above blends i.e., one could make a blend of PPQ/cellulose acetate/and polyvinylpyrrolidone, etc. This combination of three or more polymers or other possible combinations will be the subject of a further study for making polymeric membranes.

SUMMARY

Compatibilization of PPQ polymer with other polymers such as polyvinylacetate (low, medium and high molecular weight), polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymer, polybrene, cellulose acetate and cellulose triacetate was accomplished by using chloroform as the solvent medium. The above solution blends are used to prepare polymeric membranes that may be useful as battery separators.

DISTRIBUTION

NAME	COPIES
Naval Sea Systems Command Washington, D. C. 20362 Attention: Code SEA 09G32	2
Code SEA 03B	1
Code SEA 0331J (S. J. Matesky)	1
Code SEA 0331 (J. W. Murrin)	1
Code SEA 0841B (J. R. Cipriano)	1
Office of Naval Research Washington, D. C. 20360 Attention: Library	1
Office of Naval Research 800 N Quincy Street Arlington, VA 22217 Attention: Code 472 (Dr. G. A. Neece)	1
Naval Research Laboratory Washington, D. C. 20390 Attention: Code 6170 (A. C. Simon)	1
Defense Nuclear Agency Washington, D. C. 20301 Attention: Library	1
Headquarters, USAFSS Airforce Special Communications Center San Antonio, TX 78243 Attention: Library	1
Defense Documentation Center Cameron Station Alexandria, VA 22314	12
Headquarters, US Army Development & Readiness Command 5001 Eisenhower Avenue Alexandria, VA 22333 Attention: Code DRCDE-L (J. W. Crellin)	1

US Army Electronics Command	
Fort Monmouth, NJ 07703	
Attention: Code DRSEL-TL-P (D. Linden)	1
Code DRSEL-TL-PR (Dr. S. Gilman)	1
Naval Weapons Center	
China Lake, CA 93555	
Attention: Dr. Aaron Fletcher	1
US Army Mobility Equipment R & D Command, Electrochemical Div	
Fort Belvoir, VA 22060	
Attention: Code DRDME-EC	1
Naval Ship Engineering Center	
Washington, D. C. 20362	
Attention: Code 6157D (A. Himy)	1
Naval Intelligence Support Center	
4301 Suitland Road	
Washington, D. C. 20390	
Attention: Code 362 (Dr. H. E. Ruskie)	1
Naval Material Command	
Washington, D. C. 20360	
Attention: Code NAVMAT 0323 (I. Jaffe)	1
Code NAVMAT 03533 (R. H. Abrams)	1
National Aeronautics and Space Administration	
Washington, D. C. 20546	
Attention: Library	1
Naval Ocean Systems Center	
San Diego, CA 92132	
Attention: Library	1
EIC Corporation	
55 Chapel Street	
Newton, MA 02158	
Attention: J. R. Driscoll	1
Naval Underwater Systems Center	
Newport, Rhode Island 02840	
Attention: Code 3642 (T. Black)	1
Union Carbide, Nuclepore Corporation	
7035 Commerce Circle	
Pleasantown, CA 94566	
Attention: Library	1

Naval Air Systems Command Department of the Navy Washington, D. C. 20361 Attention: Code NAVAIR 310C (Dr. H. Rosenwasser)	1
Harry Diamond Lab Chief, Power Supply Branch 2800 Powder Mill Road Adelphi, MD 20783 Attention: Code DRXDO-RDD (A. A. Benderly)	1
Catholic University Chemical Engineering Department Washington, D. C. 20064 Attention: Dr. C. T. Moynihan)	1
David W. Taylor Naval Ship R & D Ctr. Annapolis Laboratory Annapolis, MD 21402 Attention: Code 2723 (A. B. Neild) Code 2724 (J. Woerner)	1 1
Naval Electronics Systems Command Washington, D. C. 20360 Attention: Code PME 124-31 (A. H. Sobel)	1
John Hopkins Applied Physics Lab John Hopkins Road Laurel, MD 20810 Attention: Library	1
Catalyst Research Corp. 1421 Clarkview Road Baltimore, MD 21209 Attention: George Bowser	1
Headquarters, Dept. of Transportation US Coast Guard, Ocean Engineering Division Washington, D. C. 20590 Attention: Code GEOE-3/61 (R. Potter)	1
Edgewood Arsenal Aberdeen Proving Ground, MD 21010 Attention: Library	1
AF Aero Propulsion Lab Wright-Patterson AFB, OH 45433 Attention: Code AFAPL/POE-1 (W. S. Bishop) Code AFAPL/POE-1 (J. Lander)	1 1

NASA Goddard Space Flight Center
Greenbelt, MD 20771
Attention: Code 711 (G. Halpert) 1

NASA Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44135
Attention: Code MS 309/1 (Dr. J. S. Fordyce) 1

Frank J. Seiler Research Laboratory
AFSC, USAF Academy, CO 80840
Attention: Code FJSRL/NC (Capt. J. K. Erbacher, USAF) 1

Naval Weapons Support Center
Electrochemical Power Sources Division
Crane, IN 47522
Attention: Code 305 (D. G. Miley) 1

Energy Research & Development Administration
Division of Electric Energy Systems
Room 2101
Washington, D. C. 20545
Attention: L. J. Rogers 1

Energy Research & Development Administration
Division of Applied Technology
Washington, D. C. 20545
Attention: Code M/S E-463 (Dr. A. Langrebe) 1

Strategic Systems Project Office
Engineering Development Project Office
Washington, D. C. 20360
Attention: Code NSP-2721 (K. N. Boyley) 1

TO AID IN UPDATING THE DISTRIBUTION LIST
FOR NAVAL SURFACE WEAPONS CENTER, WHITE
OAK LABORATORY TECHNICAL REPORTS PLEASE
COMPLETE THE FORM BELOW:

TO ALL HOLDERS OF NSWC/WOL TR 77-118
by Isaac Angres, Code CR-33
DO NOT RETURN THIS FORM IF ALL INFORMATION IS CURRENT

A. FACILITY NAME AND ADDRESS (OLD) (Show Zip Code)

NEW ADDRESS (Show Zip Code)

B. ATTENTION LINE ADDRESSES:

C.

☐ REMOVE THIS FACILITY FROM THE DISTRIBUTION LIST FOR TECHNICAL REPORTS ON THIS SUBJECT.

D.

NUMBER OF COPIES DESIRED